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14. ABSTRACT This slide presentation summarizes the results of natural attenuation treatability studies at 14 Air Force sites contaminated with chlorinated solvents and their associated biodegradation daughter products (chlorinated aliphatic hydrocarbons [CAHs]) or a mixture of solvents and other contaminants (principally fuels). The main emphasis of the work described in this report was to evaluate the potential for naturally occurring degradation mechanisms to reduce the concentrations of CAHs dissolved in groundwater to levels that are protective of human health and the environment, and to limit the migration of CAH plumes in groundwater.					
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Natural Attenuation of Chlorinated Solvents - Performance and Cost Results from Multiple Air Force Demonstration Sites

Presented by
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Parsons
Parsons engineering science, inc.

AFCOE Natural Attenuation Initiative – Chlorinated Solvents

- **Began in 1995**
- **Total of 13 Sites were Evaluated Across the Country**
- **Additional Sites were Evaluated under the Risk-Based Corrective Action Program (Travis AFB) and Other Programs (Williams AFB and MMR)**

Air Force Natural Attenuation Initiative for Chlorinated Solvents



- CAH Natural Attenuation Site
- ▲ Risk-Based Corrective Action Site

Project Elements

- **Site Visit/Kickoff Meeting**
- **Site-Specific Work Plan**
- **Field Site Characterization (Geoprobe® or CPT rig)**
- **Data Interpretation**
- **Contaminant Fate and Transport Modeling**
- **Treatability Study Report**
- **Final Regulatory Meeting**

Groundwater Analytical Protocol

Developed by AFCEE

- Contaminants/
Daughter Products
- Dissolved Oxygen
- Nitrate/Nitrite
- Fe(II)
- Sulfate/Sulfide
- Methane
- Oxidation/Reduction
Potential (ORP)
- Carbon Dioxide
- Alkalinity
- pH
- Temperature
- Total Organic
Carbon^{a/}
- Ethene/Ethane^{a/}
- Chloride^{a/}
- Hydrogen^{a/}

a/ Chlorinated Solvents Only

Wide Range of Site Characteristics

- **Depths to groundwater ranging from 0 to 60 feet bgs**
- **Plume areas ranging from 1.6 to 210 acres**
- **Average groundwater temperatures ranging from 9.1 to 25.6 °C**
- **Aquifer matrices ranging from clay to coarse sand and gravel**
- **TCE most pervasive, followed by cis-1,2-DCE**

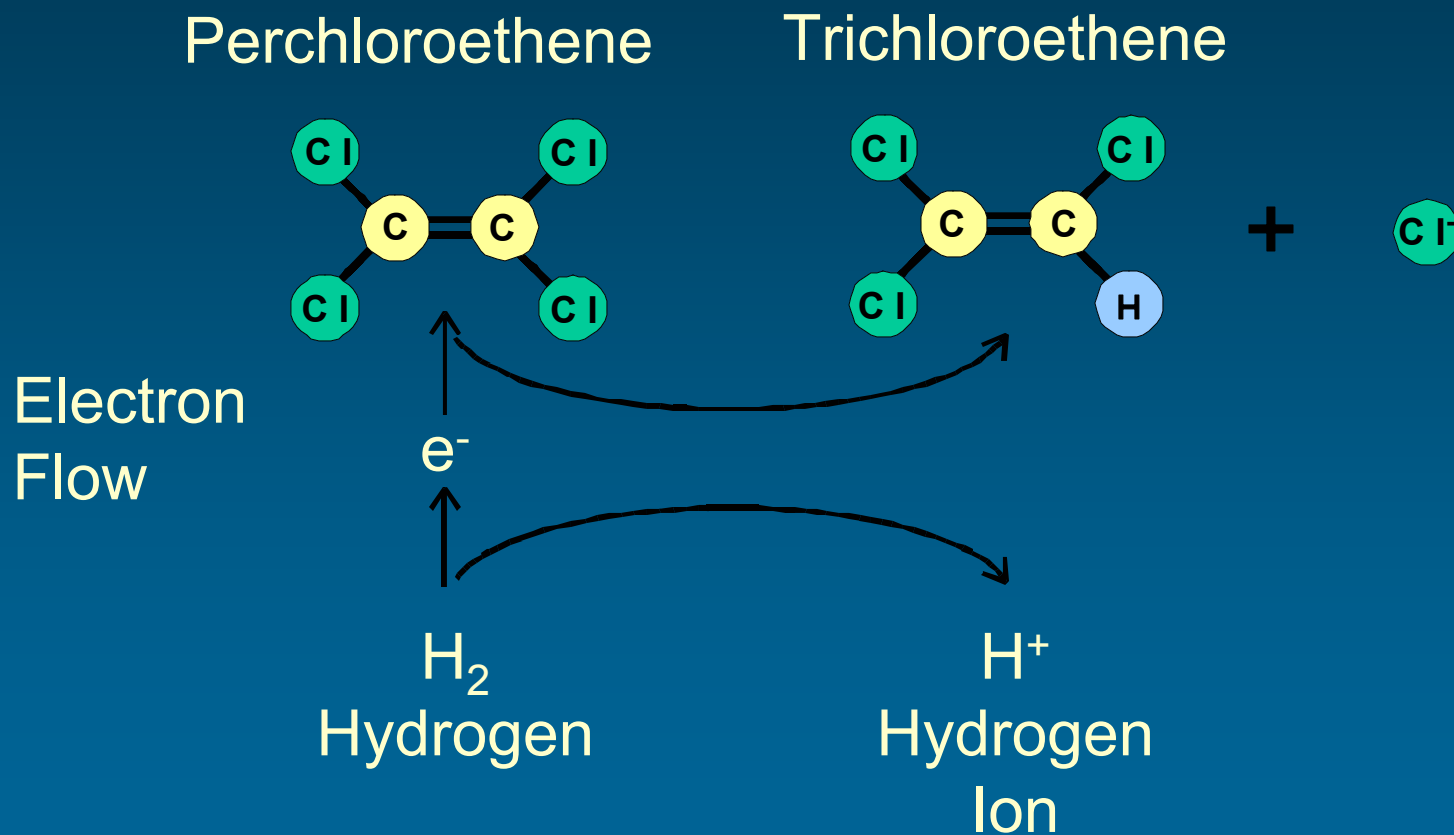
What Did We Learn from all This Variability?

- **Solvent Plumes are Like Children, Each one is Different**
- **Plume Behavior (i.e., stable, shrinking, growing) Depends on Prevailing Groundwater Geochemistry**
- **Why?**

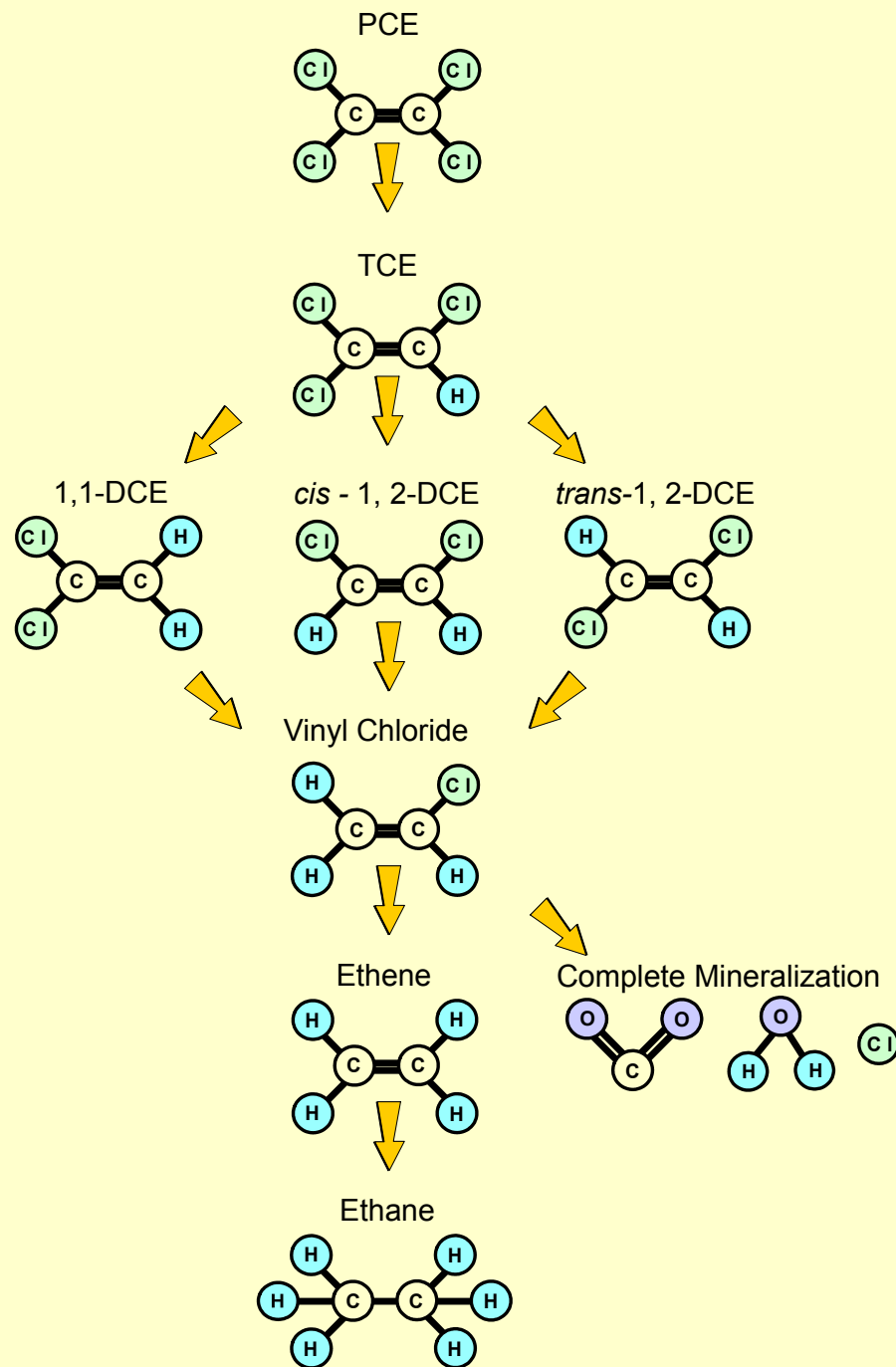
Because

- **The Common Chlorinated Solvents, PCE, TCE, Carbon Tetrachloride, and 1,1,1-TCA Predominantly Biodegrade in the Natural Environment via a process Called Reductive Dechlorination**

Reductive Dechlorination



Anaerobic Reductive Dehalogenation



Requirements for Reductive Dechlorination

- Reductive Dechlorination only Occurs Under very Strongly Reducing (Anaerobic) Conditions (e.g. Sulfate Reducing or Methanogenic)
- What is required for Strongly Reducing Conditions?
 - **A Source of Oxidizable Organic Carbon**

Effect of Prevailing Groundwater Geochemistry

- **The Presence and Amount and Type of Oxidizable Organic Carbon Determines how a Solvent Plume Behaves in Groundwater**
- **Based on AFCEE's Experience at Multiple Air Force Bases, it was determined that Plume Behavior Could be Grouped into Three Categories**

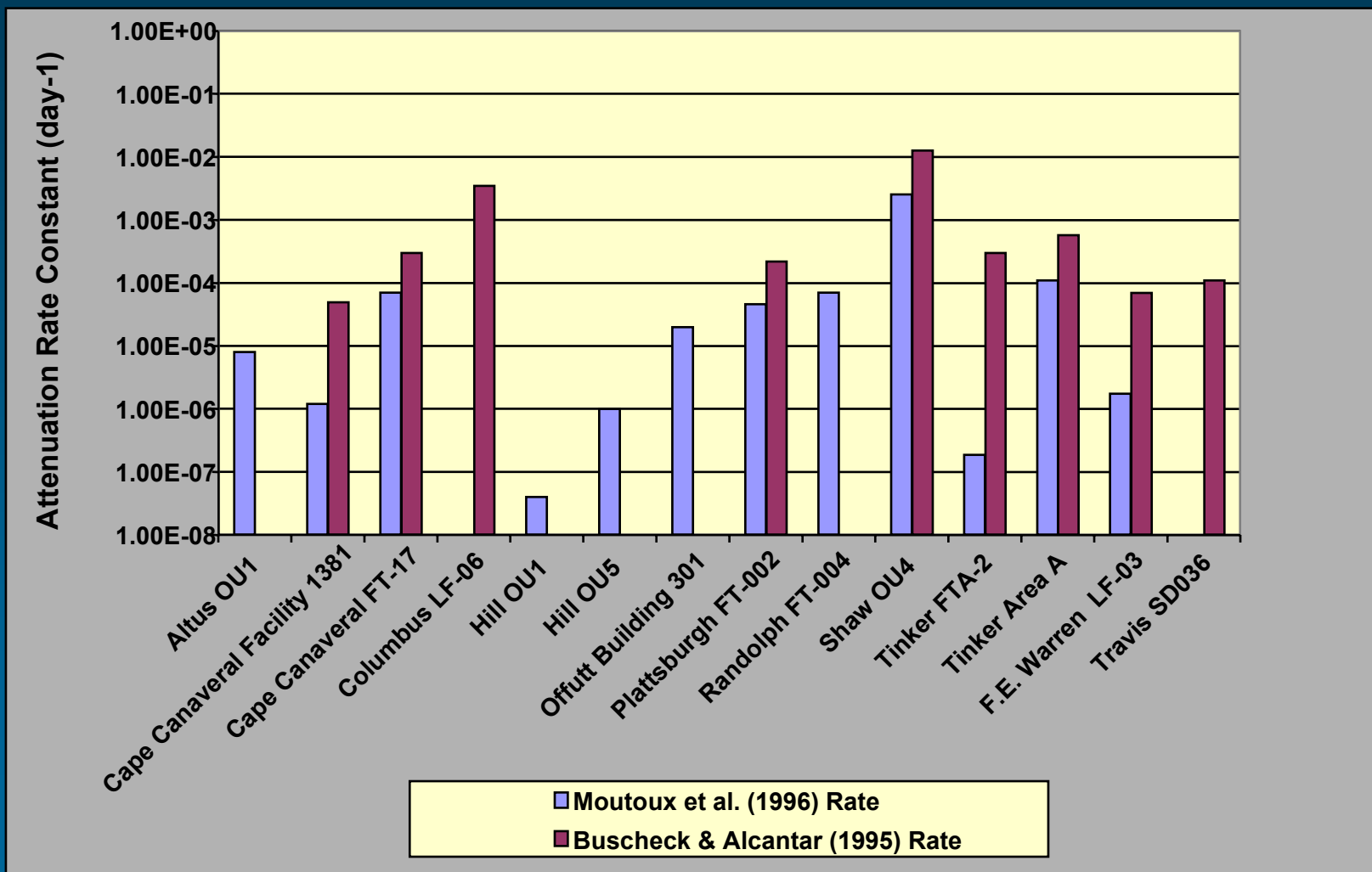
Wide Range of Plume Behavior

- **Type 1** - anthropogenic carbon drives reductive dechlorination
- **Type 2** - native organic carbon drives reductive dechlorination
- **Type 3** - low carbon levels, little or no reductive dechlorination
 - **Nine sites had a mixture of Type 1 plus Type 2 or 3; two sites with mixture of Type 2 and 3, three sites with primarily Type 1**

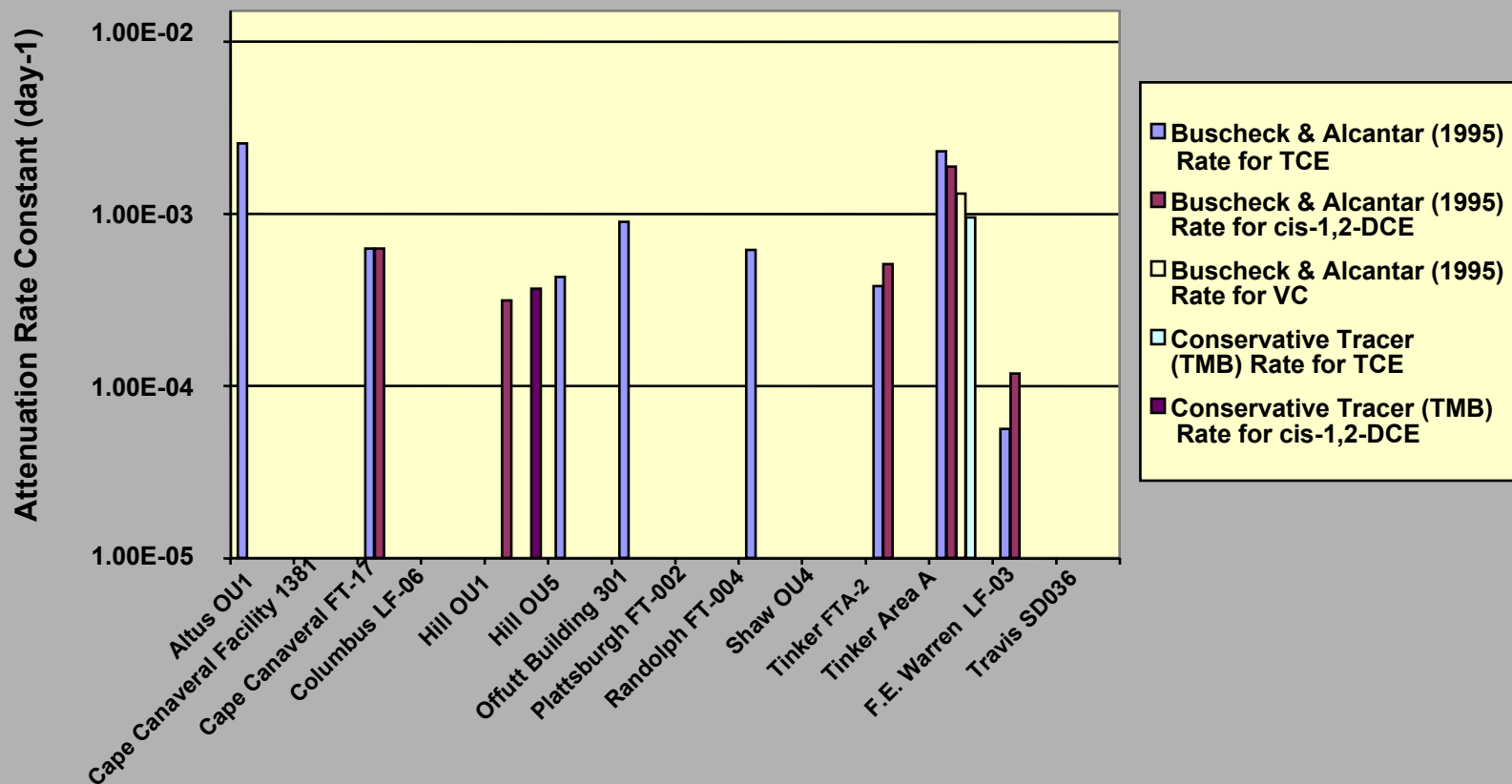
Calculation of Field Biodegradation Rates

- **Use of a biologically conservative tracer**
- **Method of Buscheck & Alcantar (1995) for steady-state plumes**
- **Method of Moutoux *et al.* (1996)**

Estimated Attenuation Rates for Total Chlorinated Ethenes



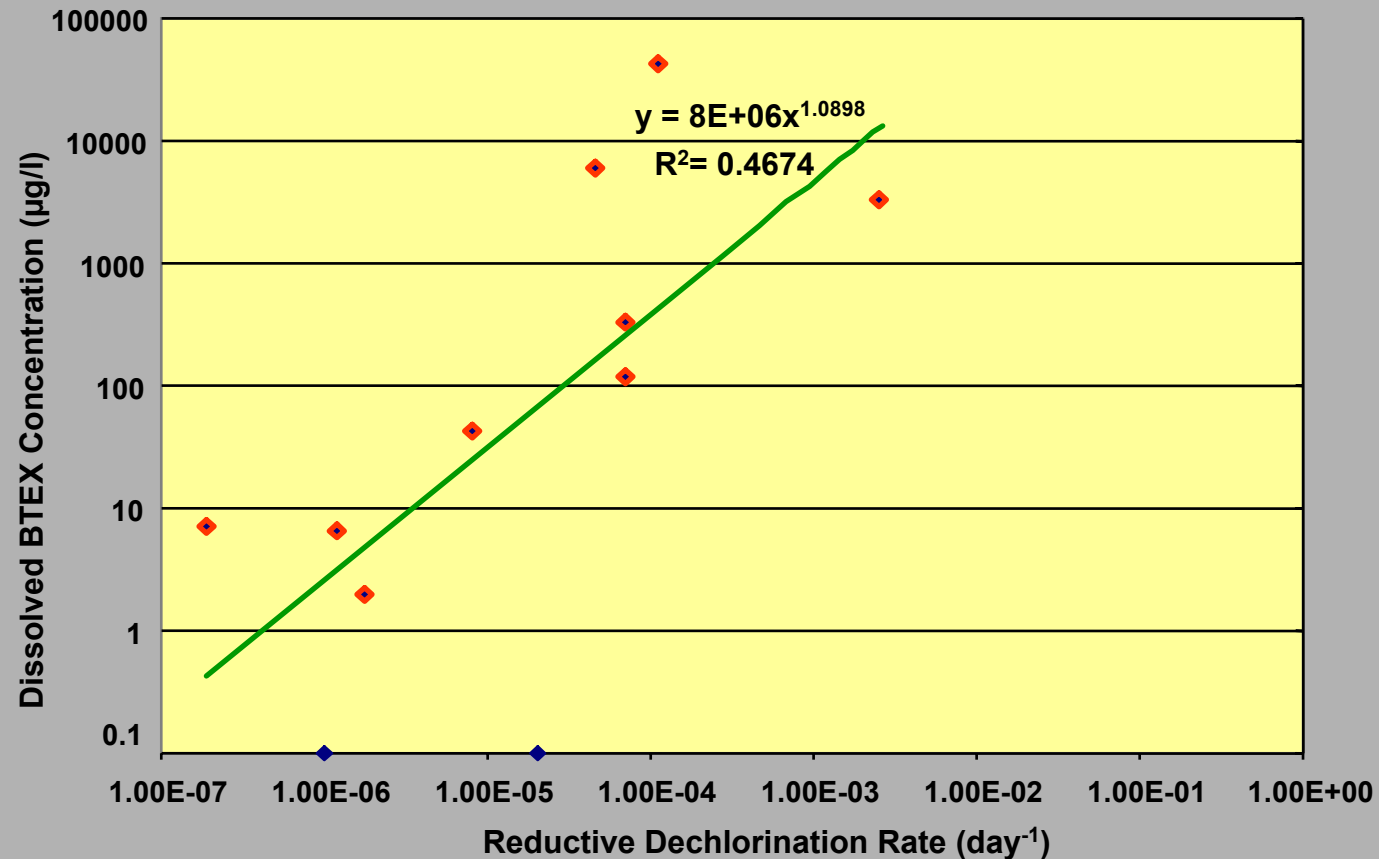
Estimated Attenuation Rates for TCE, DCE, and VC



Summary of Total Destructive Attenuation Rates

<u>Compounds</u>	<u>No. of Rates</u>	<u>Geometric Mean (day⁻¹)</u>	<u>Half-Life (yr)</u>	<u>Median (day⁻¹)</u>	<u>Half-Life (yr)</u>
Total Chlorinated Ethenes	8 (B&A)	4.0×10^{-4}	4.7	2.6×10^{-4}	7.3
Trichloroethene	5 (B&A)	5.2×10^{-4}	3.7	5.0×10^{-4}	3.8 (0.4)*
	1 (TMB)	7.0×10^{-4}	2.7		
cis-1, 2-Dichloroethene	4 (B&A)	3.7×10^{-4}	5.1	3.8×10^{-4}	5.0 (0.5)*
	1 (TMB)	3.0×10^{-4}	6.3	—	—
Vinyl Chloride	1 (B&A)	1.0×10^{-4}	1.9	1.0×10^{-4}	1.9 (0.4)*

Maximum BTEX Concentration vs. Biodegradation Rate



Solute Fate and Transport Modeling

- **Numerical Models were used to Predict the Fate and Transport of Solvents in Groundwater**
- **Modflow/MT3D**

Solute Fate and Transport Modeling

- **Out of 13 Plumes Models Predicted:**
 - **2 Plumes at Steady-State**
 - **1 Plume Expanding Along Sewer Line Corridors**
 - **4 Plumes Discharging to a Surface Water Body**
 - **6 Plumes Expanding (250 to 9,500 ft)**

Predicted CAH Plume Persistence

- **Estimated time required for natural attenuation alone to achieve cleanup goals:**
 - **17 to >200 years**
 - **>100 years for 6 of 12 sites**

Predicted CAH Plume Persistence

- If engineered source reduction and/or hotspot pumping performed, predicted cleanup times exceeded lengths of simulation periods (35-200 years) at 6 of 11 sites; timeframe decreased 0 to 90% (avg 44%) at remaining 5 sites

Conclusions from Modeling Effort

- **In Many Cases, Groundwater Quality Standards may not be Achieved within 100 years Without Aggressive Remedial Actions in the Source Area**

Conclusions from Modeling Effort

- **In Some Cases, Soil Remediation has Minimal Impact on the Total Time Frame Required for Natural Attenuation to Achieve Cleanup Goals for Groundwater**

Modeling Limitations

- **Available Models used First-Order Decay Rates**
- **Source Characteristics, History, and Weathering Rate Often Unknown-- Simulated as “Black Box”**

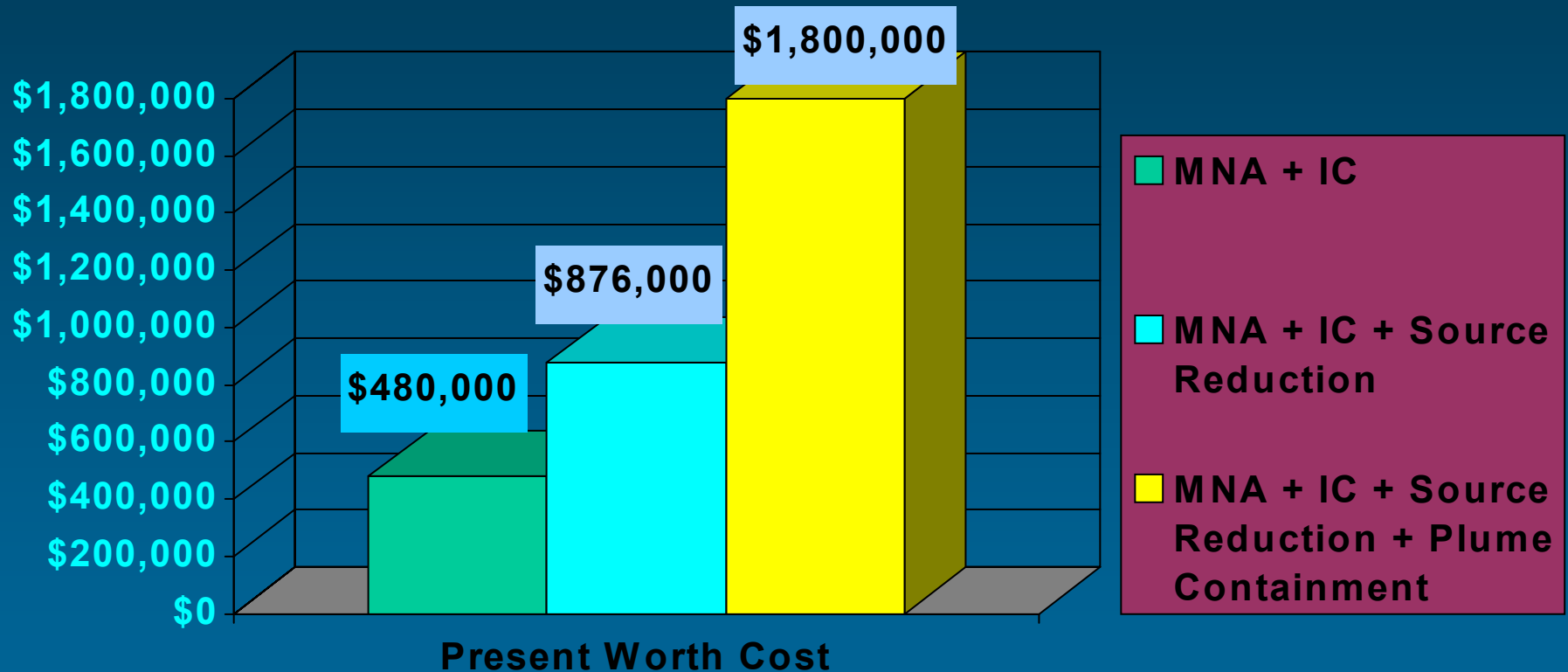
Modeling Limitations

- **Fate and Transport of Parent and Daughter Compounds Could not be Simulated Simultaneously**
- **Earlier Model Versions did not Allow Spatial Variability of Input Parameters**

Proposed Remedial Alternatives

- **MNA +IC: 2 sites (out of 14)**
- **MNA, IC, + engineered source reduction and/or hotspot pumping: 7 sites**
- **MNA, IC, + downgradient plume cutoff: 4 sites**
- **Insufficient data for recommendation: 1 site**

Remedial Alternative Cost Comparisons



Long-Term Monitoring

- Recommended number of LTM wells ranged from 8 to 30 and averaged 17
- LTM of surface water recommended at 9 sites
- Recommended sampling frequencies ranged from 1 to 2 years (annual sampling most frequently recommended)

Typical Natural Attenuation Treatability Study Costs

<u>Task</u>	Geoprobe®/Cone Penetrometer
Site Visit/Technical Support ^{a/}	\$9,010
Work Plan/Regulatory Approval ^{b/}	\$20,300
Field Work Labor	\$9,760
Field Work Other Direct Costs (ODCs)	
Survey/Supplies/Per Diem	\$6,150
Geoprobe®/Cone Penetrometer Operation	\$878
Data Analysis/Analytical	\$18,200
Total Field Work ODCs	\$25,300
Modeling	\$19,400
Treatability Study Report ^{c/}	\$38,100
Total Project	\$122,000

a/ Includes kickoff meeting, post-reporting meeting, and regulatory support.

b/ Includes draft and final versions, and gathering/analyzing available site data.

c/ Includes draft and final versions, with formal written responses to review comments on the draft report.

Findings of Natural Attenuation Evaluations - Solvents

- **Intrinsic Bioremediation Occurring at Approximately 88% of the Sites Studied (Biased, Probably 40%)**
- **Reductive Dechlorination Occurring at 100% of Sites Impacted with Fuels**
- **Surface Water Impacted at Many Sites**
- **6 of 13 Plumes Expected to Grow**

What Does all of This Mean?

- **Some Form of Engineered Remediation may be Required at Many Sites**
- **Is Pump and Treat the Answer?**
- **ABSOLUTELY NOT!!!**
- **Why?**

Engineered Bioremediation of Chlorinated Solvents

- **Because Pump and Treat is Expensive and Doesn't Work**
- **The Limiting Factor at Many Sites Contaminated with Chlorinated Solvents is the Lack of Suitable Oxidizable Organic Carbon**

Engineered Bioremediation of Chlorinated Solvents

- **Many Types of Organic Substrate Have Been Added to Groundwater to Stimulate Biodegradation of Solvents Including:**
 - **Propionate**
 - **Lactate**
 - **Butyrate**
 - **Molasses**
 - **Hydrogen Releasing Compound[®]**
 - **Hydrogen (“Hindenberg Experiment”)**

Engineered Bioremediation of Chlorinated Solvents

- **All of These Materials are Added to Stimulate the Production of Hydrogen for Reductive Dechlorination**
- **All are Soluble to Some Extent in Water and Many are Miscible**
- **This Means Continuous Injection or at a Minimum, Multiple Injections (With the Exception of HRC[®])**

VegOil for Engineered Bioremediation of Chlorinated Solvents

- **Injection of Food-Grade Vegetable Oil as a Carbon Substrate Looks Promising**
- **VegOil is a Non Aqueous Phase Which Means one Time Injection and Slow Dissolution**

Conclusions and Recommendations

- **The Air Force Should Require Evaluation of Natural Attenuation Before Considering Other Alternatives**
- **State-of-the-art Modeling Software and “Realistically Conservative” Assumptions Should be Used to Obtain More Plausible Results and Facilitate Evaluation of Remedial Alternatives**

Conclusions and Recommendations

- **Pounds of Contaminants Removed via Natural Attenuation Alone Should be Compared Against other Remedial Alternatives – People Will be Amazed**
- **If Engineered Remediation is Required the Focus Should be on In Situ Source Reduction Techniques**

Recommendations (continued)

- **More Costly Remediation Techniques Should be Considered only if the Plume Poses a Threat to Human Health or the Environment**
- **Hot-Spot Pumping or Air Sparging may Result in Aerobic Groundwater Conditions – Could Ruin the Natural Treatment System**